

Theoretical T_1 Calculation for Isotropic High Spin Molecules

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Abstract

We calculate the molecular-spin (S), temperature (T), and field (H) dependence of $1/T_1$ for a local magnetic probe coupled to an isotropic high spin molecule, based on spin-phonon interaction. We compare the calculation to recent NMR and μ SR experiments in CrCu_6 ($S = 9/2$), CrNi_6 ($S = 15/2$) and CrMn_6 ($S = 27/2$). Although we can account for the high and intermediate temperature regimes, the calculation is fundamentally different from the data at $T \rightarrow 0$. Since $1/T_1$ must be due to coupling of the molecular spin to an external heat bath, and since phonon contribution is ruled out at low T , we conclude that at these temperatures hyperfine interactions must play an important role in the molecular spin dynamic.

I. INTRODUCTION

High spin molecules (HSM) consist of clusters of metal ions, they are ordered in a crystal lattice, and coupled by Heisenberg ferromagnetic or anti-ferromagnetic interactions with coupling constant J , only between spins \vec{S}_i in the molecule. In this paper we study a family of isotropic high spin molecules. We calculate the spin lattice relaxation $1/T_1$ in these molecules, and compare it to experimental measurements¹ to determine the origin of the observed spin dynamics of the molecules. We find that at high temperature the molecular spin dynamics is driven by thermal activation (spin-phonon interaction). However at low temperatures the molecular spin dynamics is dominated by hyperfine interactions between the molecular and nuclear spin.

These calculations can be easily applied to different kinds of high spin molecules, such as Mn_{12} ^{2,3,4} and Fe_8 ⁵, where quantum tunneling of the magnetization (QTM) is observed^{3,4,5}. Comparison between experimental measurements^{6,7} and the calculation can help determine which interactions induce the spin tunneling in these molecules.

In the isotropic molecules a Cr(III) ion is surrounded by six cyanide ions, each bonded to a Cu(II), Ni(II) or Mn(II) ion. The coordination sphere of Cr and Cu/Ni/Mn can be described as a slightly distorted octahedral. For convenience we will refer to these molecules as CrCu_6 , CrNi_6 and CrMn_6 , respectively. The Hamiltonian of the isotropic high spin molecules at zero field can be written as

$$\mathcal{H}_0 = -J \sum_{i=1}^6 \vec{S}_0 \cdot \vec{S}_i \quad (1)$$

where \vec{S}_0 is the spin of the central Cr ion (with $S = 3/2$), i runs over the peripheral Cu, Ni or Mn ions (with $S = 1/2$, $S = 1$ or $S = 5/2$), which are coupled to the central Cr ion, with coupling constant J (e.g. see Figure 1). At temperatures lower than J only the ground spin state $S = 9/2$, $S = 15/2$ or $S = 27/2$ is populated.

The Hamiltonian \mathcal{H}_0 is isotropic therefore the total spin S and the spin in the z direction m are good quantum numbers, and the eigenfunctions of \mathcal{H}_0 can be written as $|S, m\rangle$. However, at very low temperatures $T \ll J$, the degeneracy of the ground state is removed by additional anisotropic perturbation on \mathcal{H}_0 . Such perturbation that does not commute with \mathcal{H}_0 can cause transitions between the different spin states $|S, m\rangle$ ^{1,8,9,10,11,12,13,14,15,16,17}, and induce the observed spin dynamics^{1,15}.

The anisotropic term in the Hamiltonian can be written as the sum $\mathcal{H}' = \mathcal{H}_c + \mathcal{H}_n$, where

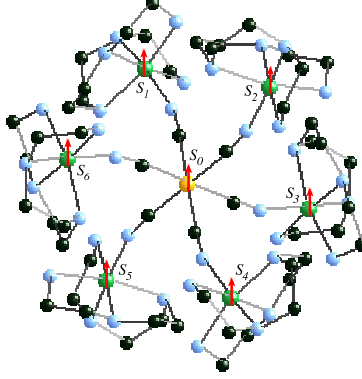


FIG. 1: The magnetic core of the CrNi_6 molecule, S_0 is the spin of the Cr ion and S_1, S_2, \dots, S_6 are the spins of the Ni ions.

\mathcal{H}_c commutes with the Hamiltonian \mathcal{H}_0 , while \mathcal{H}_n does not. These terms may be a result of dipolar interaction between neighboring spins^{8,16}, spin-phonon interaction^{13,17}, nuclear fluctuations¹⁴, high order crystal field terms^{5,8,9,10,11,12} or small anisotropy in the coupling J between spins¹⁸.

In order to calculate the value of the spin lattice relaxation time T_1 in the isotropic HSM we diagonalize the Hamiltonian $\mathcal{H}_0 + \mathcal{H}_c$ in Section II. In Section III we show that we can calculate the magnetization and susceptibility of the compounds using the eigenvalues and eigenfunctions that we obtain. In Section IV we use the eigenvalues and eigenfunctions of the Hamiltonian to calculate T_1 , taking \mathcal{H}_n as a perturbation. The perturbation introduces a finite lifetime for the different spin states $|S, m\rangle$ and induces spin dynamics, or transitions between the different spin states.

II. EXACT DIAGONALIZATION OF THE HAMILTONIAN

To calculate the eigenvalues of the Hamiltonian (1) we write it in the form

$$\mathcal{H}_0 = -J\vec{S}_0 \cdot \sum_{i=1}^6 \vec{S}_i. \quad (2)$$

Using $\vec{S} = \vec{S}_0 + \sum_{i=1}^6 \vec{S}_i$ and $\vec{S}_t = \sum_{i=1}^6 \vec{S}_i$ one can write

$$\mathcal{H}_0 = -J\vec{S}_0 \cdot \vec{S}_t = -\frac{J}{2} (\vec{S}^2 - \vec{S}_t^2 - \vec{S}_0^2). \quad (3)$$

The energy eigenvalues of the states $|S, m\rangle \equiv |S_0, S_t, S, m\rangle$ are

$$E_{\mathbf{S}} \equiv E(S, S_t, S_0) = -\frac{J}{2} (S(S+1) - S_t(S_t+1) - S_0(S_0+1)) \quad (4)$$

where we use the notation \mathbf{S} for the set of numbers (S, S_t, S_0) . The degeneracy of the state $|S, m\rangle$ is the degeneracy of the value of S_t . When an external magnetic field H is applied the Zeeman term should be added to \mathcal{H}_0 , and the full Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_0 - g\mu_B H S_z, \quad (5)$$

for which the eigenfunctions $|S, m\rangle$ are not changed and the eigenvalues are

$$E_{\mathbf{S},m} = -\frac{J}{2} (S(S+1) - S_t(S_t+1) - S_0(S_0+1)) - g\mu_B H m. \quad (6)$$

In Figure 2 we present the energy levels of CrNi_6 at zero magnetic field $H = 0$ as a function of the total spin S (a) and as a function of the spin in z direction m (b).

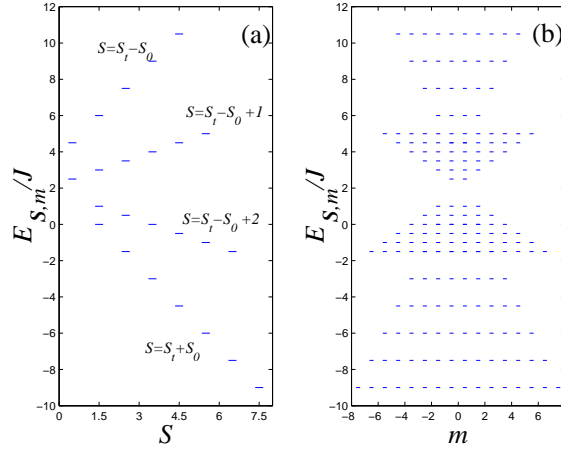


FIG. 2: The energy levels of the Hamiltonian \mathcal{H}_0 at zero field for CrNi_6 as a function of (a) the total spin S and (b) the spin in the z direction m .

III. SUSCEPTIBILITY CALCULATION

The susceptibility can be calculated as a function of temperature and external field using the eigenstates and eigenvalues that we calculated in the previous section. First we calculate the magnetization

$$M(T) = \langle S_z \rangle = \sum_{|S,m\rangle} \frac{m e^{-\frac{E_{\mathbf{S},m}}{T}}}{\mathcal{Z}} \quad (7)$$

where $\mathcal{Z} = \sum_{|S,m\rangle} \exp\left(-\frac{E_{\mathbf{S},m}}{T}\right)$ is the partition function. The measured susceptibility¹ is defined as

$$\chi(T) = \frac{M(T)}{H}. \quad (8)$$

In Figure 3 we fit the experimental measurement of χT as a function of temperature in (a) CrCu_6 , (b) CrNi_6 and (c) CrMn_6 , at fields $H = 100$ G and 2.15 T, to the calculated value of χT from the Hamiltonian (5) and Eq. (8). From the fit one obtains the coupling constants $J_{\text{Cr-Cu}} = 77$ K, $J_{\text{Cr-Ni}} = 24$ K and $J_{\text{Cr-Mn}} = -11$ K and no anisotropy is observed in all three molecules, within the fitting accuracy. This indicates that the high spin molecules can

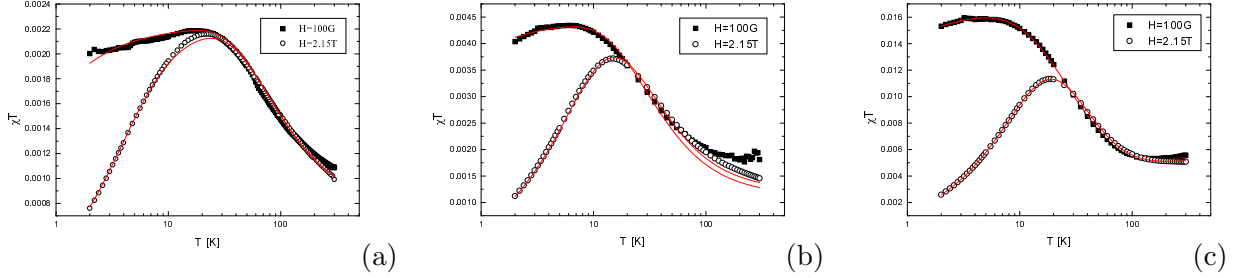


FIG. 3: The susceptibility multiplied by temperature as a function of temperature at two different external fields, measured in (a) CrCu_6 (b) CrNi_6 and (c) CrMn_6 . The solid lines are fits to the theoretical expectation (see text).

be well described by the Hamiltonian (5), and that the molecules are indeed isotropic.

IV. T_1 CALCULATION

The spin lattice relaxation time T_1 was measured¹ in CrCu_6 , CrNi_6 and CrMn_6 using μSR (where the local probes are polarized muons) and proton-NMR. Assuming for simplicity an isotropic interaction between the probe \vec{I} (muon or proton) and the local electronic spins \vec{S} of the whole molecule

$$\mathcal{H}_{IS} = A\vec{I} \cdot \vec{S} \quad (9)$$

the spin lattice relaxation is given by¹⁹

$$\frac{1}{T_1} = \frac{A^2}{2} \int_{-\infty}^{\infty} \langle S_-(t)S_+(0) \rangle e^{i\omega t} dt \quad (10)$$

where $\omega = \gamma H$ is the probe's Larmor frequency in an external field H . The value of

$$\langle S_-(t)S_+(0) \rangle = \left\langle e^{-i\mathcal{H}t/\hbar} S_- e^{i\mathcal{H}t/\hbar} S_+ \right\rangle$$

for the eigenstates $|S, m\rangle$ of the Hamiltonian \mathcal{H} in Eq. (5) is,

$$\langle S_-(t)S_+(0) \rangle = \sum_{|S, m\rangle} (S(S+1) - m(m+1)) e^{i\left(\frac{E_{S, m+1} - E_{S, m}}{\hbar}\right)t} \frac{e^{-\frac{E_{S, m}}{T}}}{Z}$$

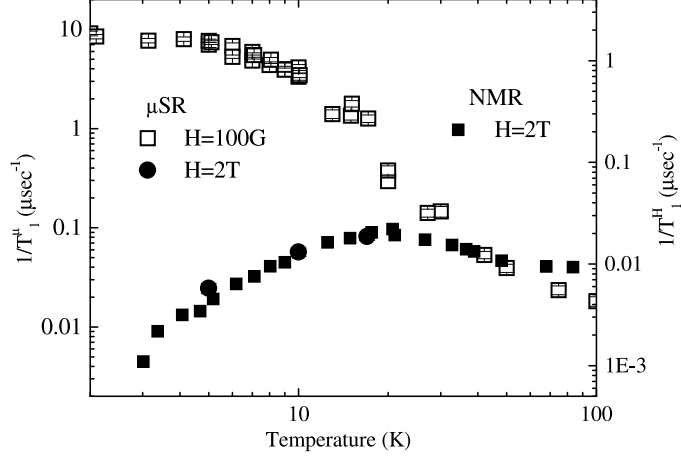


FIG. 4: The values of the spin lattice relaxation measured by μ SR ($1/T_1^\mu$), compared to those measured by proton NMR ($1/T_1^H$) after scaling, at the same external field $H = 2.15$.

where \mathcal{Z} is the partition function. This result is correct for a system with levels of infinitely long lifetime. However, assuming a Lorentzian broadening of the levels, due to the non-commuting additional terms in the Hamiltonian, \mathcal{H}_n , we arrive at

$$\langle S_-(t)S_+(0) \rangle = \sum_{|S,m\rangle} \frac{e^{-\frac{E_{S,m}}{T}}}{\mathcal{Z}} (S(S+1) - m(m+1)) e^{-\frac{t}{\tau_{S,m}}} e^{i\left(\frac{E_{S,m+1} - E_{S,m}}{\hbar}\right)t} \quad (11)$$

where $\tau_{S,m}$ is the lifetime (or the inverse of the broadening) of the level $|S, m\rangle$. Hence according to Eq. (10)

$$\frac{1}{T_1} = \frac{A^2}{2} \sum_{|S,m\rangle} \frac{e^{-\frac{E_{S,m}}{T}}}{\mathcal{Z}} (S(S+1) - m(m+1)) \int_{-\infty}^{\infty} e^{-\frac{t}{\tau_{S,m}}} e^{i\omega' t} dt \quad (12)$$

where $\omega' = \omega + (E_{S,m+1} - E_{S,m})/\hbar$. The energy difference in our case of isotropic molecules is $E_{S,m+1} - E_{S,m} = -g\mu_B H$, therefore $\omega' = \omega - \frac{g\mu_B}{\hbar} H$ and

$$\frac{1}{T_1} = \frac{A^2}{2\mathcal{Z}} \sum_{|S,m\rangle} (S(S+1) - m(m+1)) \left(\frac{\tau_{S,m} e^{-\frac{E_{S,m}}{T}}}{1 + \omega'^2 \tau_{S,m}^2} \right), \quad (13)$$

in contrast to what was obtained in⁷, where the term $(S(S+1) - m(m+1))$ is missing in Eq. (13) and ω' is replaced by $\omega = \gamma H$.

This result is important for understanding of the comparison between the spin lattice relaxation rate measured by μ SR and NMR at $H = 2.15$ Tesla, shown in Figure 4. The field dependence of $1/T_1$ comes from $\omega' = (\gamma - g\mu_B/\hbar)H$. Since the gyromagnetic ratio γ of the probe (muon or nucleus) is much smaller than $g\mu_B/\hbar$ (electronic gyromagnetic ratio),

one can write $\omega' \simeq -g\mu_B H/\hbar$ which does not depend on the value of γ . Therefore the field dependence of the spin lattice relaxation rate $1/T_1$ is independent of the value of γ , and depends only on the value of A . This explains the fact that the spin lattice relaxation rate measured by proton-NMR can be scaled to match that measured by μ SR *at the same external field*, and not at the same Larmor frequency of the probe (see Figure 4). However, Eq. (13) is valid assuming that the perturbation \mathcal{H}_n is smaller than the Zeeman splitting, $E_{\mathbf{S},m+1} - E_{\mathbf{S},m}$, i.e. at high fields where $g\mu_B H \gg \mathcal{H}_n$. When the Zeeman splitting is smaller than \mathcal{H}_n , ω' should be replaced by $\omega = \gamma H$, in Eq. (13).

The lifetime $\tau_{S,m}$ of the level $|S, m\rangle$ can be expressed in terms of transition probability from the state $|S, m\rangle$ to another state $|S', m'\rangle$

$$\frac{1}{\tau_{S,m}} = \sum_{(S',m') \neq (S,m)} p(S, m \rightarrow S', m') \quad (14)$$

which depends only on the additional parts of the Hamiltonian \mathcal{H}_n which induce these transitions. In what follows we will try to account for this lifetime assuming different possible interactions.

A. Spin-Phonon Interaction

To account for the temperature dependence of T_1 we should take into consideration the transitions induced by spin-phonon interactions. The spin-phonon coupling Hamiltonian^{17,20}, \mathcal{H}_{sp} , can induce transitions between different spin states of the molecule. The transition rate from a state $|S, m\rangle$ to a state $|S', m'\rangle$ can be calculated using the golden rule in perturbation theory²¹

$$p(S, m \rightarrow S', m') = \frac{3}{2\pi} \frac{|\langle S, m | \mathcal{H}_{sp} | S', m' \rangle|^2}{\hbar^4 \rho c^5} (E_{\mathbf{S},m} - E_{\mathbf{S}',m'})^3 \frac{1}{\exp[(E_{\mathbf{S},m} - E_{\mathbf{S}',m'})/T] - 1} \quad (15)$$

This result involves the matrix element $\langle S, m | \mathcal{H}_{sp} | S', m' \rangle$ of the spin-phonon interaction, the phonon velocity c , the specific mass ρ and the energy difference $(E_{\mathbf{S},m} - E_{\mathbf{S}',m'})$, where it was assumed that $E_{\mathbf{S},m} > E_{\mathbf{S}',m'}$. To get the right order of magnitude, and simplify the calculations, we assume a constant spin-phonon interaction matrix element, arriving at

$$p(S, m \rightarrow S', m') = \frac{C(E_{\mathbf{S},m} - E_{\mathbf{S}',m'})^3}{\exp[(E_{\mathbf{S},m} - E_{\mathbf{S}',m'})/T] - 1} \quad (16)$$

where

$$C = \frac{3}{2\pi} \frac{|\langle S, m | \mathcal{H}_{sp} | S', m' \rangle|^2}{\hbar^4 \rho c^5}.$$

The transition probability due to spin-phonon interaction strongly depends on temperature. At very low temperature phonons die out exponentially with decreasing temperature, yielding a very low transition probability, and extremely low spin lattice relaxation rate values as seen in Figure 5. Therefore this interaction cannot give a full explanation to the nonzero spin lattice relaxation rate at low temperatures, which is observed in experiments^{1,15}, and additional terms in the Hamiltonian should be considered.

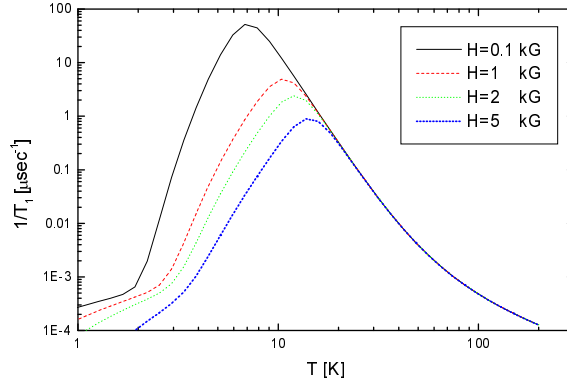


FIG. 5: Spin lattice relaxation rate as a function of temperature for different magnetic fields in CrNi₆, when assuming spin-phonon interactions only. For this figure we used $C = 400$ 1/sec K³ and $A = 5.2$ MHz in Eq. (13) and (16).

B. Other Interactions

In order to obtain a finite spin lattice relaxation rate at very low temperatures, the lifetime of the levels should be finite. This cannot be accounted for by spin-phonon interaction as seen in the previous section. A finite lifetime can be achieved if one simply assumes a finite broadening of the levels due to an additional interaction \mathcal{H}_{int} , giving a short lifetime τ_{int} for the levels. The assumption implied by the experimental results¹ is that τ_{int} is temperature and field independent at low fields.

In this case the total lifetime of the levels consists of two contributions, τ_{sp} due to spin-

phonon interaction \mathcal{H}_{sp} and τ_{int} due to the additional interaction \mathcal{H}_{int} , therefore

$$\frac{1}{\tau_{S,m}} = \left(\frac{1}{\tau_{sp}} + \frac{1}{\tau_{int}} \right). \quad (17)$$

At high temperatures the value of the spin-phonon contribution to the lifetime, τ_{sp} , is much shorter than τ_{int} and the value of T_1 is dominated by spin-phonon induced transitions, while at very low temperatures τ_{sp} is much longer than τ_{int} , and the value of T_1 is dominated by τ_{int} . At intermediate temperatures both contributions to the spin lattice relaxation are important.

In Figure 6 we present the experimental values of $1/T_1$, measured by μ SR¹, as a function of temperature at different fields, for the molecules (a) CrCu₆, (b) CrNi₆, and (c) CrMn₆. The solid lines are fits to the theoretical values expected assuming transitions which are induced by spin-phonon interaction in addition to \mathcal{H}_{int} . The fits give the parameters' values summarized in Table I.

<i>Compound</i>	τ_{int} [nsec]	C [1/sec K ³]	A [MHz]
CrCu ₆	7.0(8)	0.13(9)	1.7(1)
CrNi ₆	11.0(8)	400(60)	5.2(2)
CrMn ₆	9.1(8)	0.004(1)	4.7(2)

TABLE I: The fit parameters of the theoretical calculation of the spin lattice relaxation to the experimental values from μ SR measurements

The parameters quoted in Table I were calculated using Eq. (13) with $\omega = \gamma_\mu H$ instead of ω' , since the experimental measurements were performed at low fields. The quoted values of τ_{int} indicate that \mathcal{H}_{int} is of order of 0.7 – 1.1 K, which is larger than the Zeeman splitting in fields up to 2 kG, and self consistent with the use of Eq. (13) with $\omega = \gamma_\mu H$ instead of ω' .

The fits in Figure 6 capture the essence of the temperature and field dependence of $1/T_1$, considering the simplifications that we have used, and it gives the correct general behavior of the experimental data. However, at very low temperatures and high fields the theoretical calculation deviates from the experimental data. Similarly at high temperatures $T \gg J$, where $1/T_1$ is very small, the theoretical calculation deviates from the experimental data (especially in the case of CrNi₆). We believe that the origins of the deviation at high temperatures is that the Hamiltonian (5) does not describe the system well enough, and

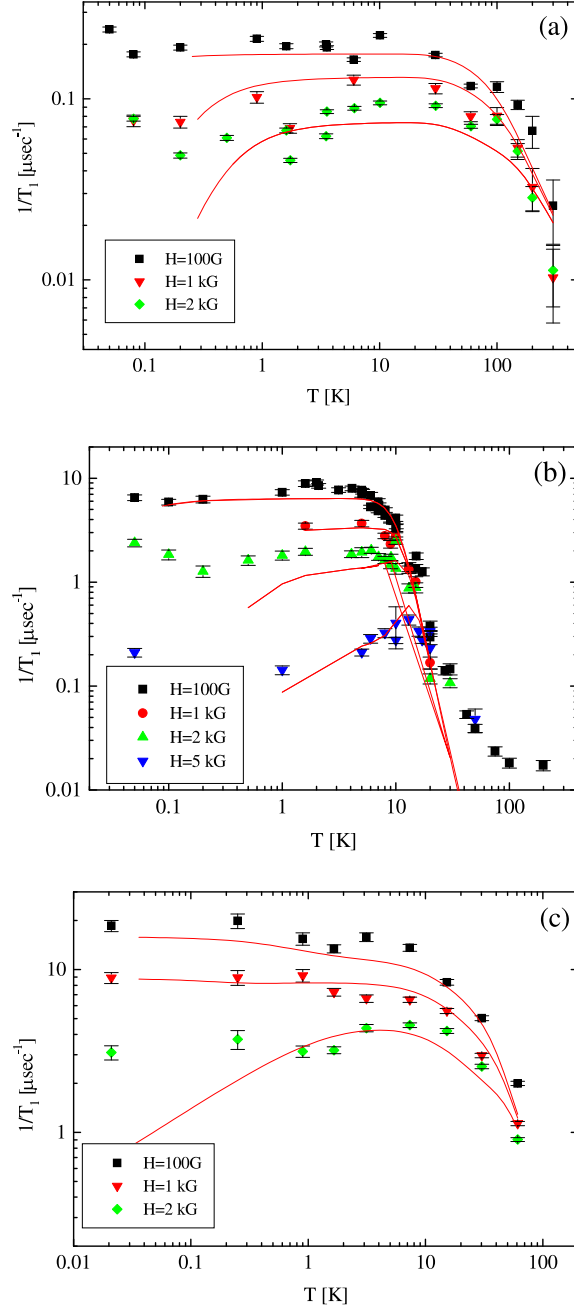


FIG. 6: The value of $1/T_1$ as a function of T at different fields, measured using μ SR in (a) CrCu_6 , (b) CrNi_6 and (c) CrMn_6 . The solid lines are fits to the calculated value (see text).

that the value of $1/T_1$ is very small and is harder to estimate experimentally. This can also be seen in Figure 3, where at high temperatures the calculated value of χT deviates from the experimental values.

V. CONCLUSION

The calculated spin lattice relaxation rate of a local probe, with gyromagnetic ratio γ , in the isotropic HSM follows Eq. (13). This result remains valid assuming an isotropic interaction between the probe's spin and the molecular spin, and assuming a finite lifetime $\tau_{S,m}$ for the spin state $|S, m\rangle$ at all temperatures and fields. Eq. (13) indicates that the spin lattice relaxation rate in these molecules is independent of the probe's gyromagnetic ratio at high magnetic fields, and therefore the measured values of spin lattice relaxation by μ SR and proton-NMR scale at the same *external field* (at high fields), and not at equal Larmor frequencies.

The calculated lifetime of the levels τ_{int} is found to vary between 7 – 11 nsec, which can be translated to a broadening of 3 – 5 mK. Therefore we expect that the interaction which introduces the spin dynamics in these molecules produces level broadening of the same order of magnitude.

The temperature and field independent levels broadening $1/\tau_{int}$ calculated above can be attributed to an interaction that does not commute with S_z and induces transitions between the different m states. This interaction can be dipolar between neighboring molecules, hyperfine between molecular and nuclear spins, crystal field higher order terms, etc. However, the striking fact is that the lifetime is similar in all three molecules, indicating that it does not depend strongly on the spin of the molecule or the coupling J between ions inside the molecule, which varies greatly between the three molecules.

This indicates that the weak dependence of the broadening on the spin value cannot be explained by interactions which are quadratic in S or have higher S dependence. This rules out dipolar interactions between neighboring molecules since in the three compounds the nearest neighbor distance is ~ 15 Å. Similarly, crystal field terms which are allowed by the octahedral symmetry (S^2 or higher²²) are unlikely.

The only mechanism suggested to date for level broadening of HSM, which depends weakly on S is the hyperfine interaction between nuclear and electronic spins. This mechanism can account for the finite spin lattice relaxation rate at very low temperatures²³. However, the values of broadening calculated above might be inaccurate due to the simplifications made in the calculations, but give the right order of magnitude expected from hyperfine interactions²⁴.

Hyperfine interactions in anisotropic high spin molecules were studied recently^{12,25}, and their effect on QTM is becoming clearer^{26,27}. We believe that this interaction also governs the spin dynamics of the isotropic molecules at very low temperatures ($T < 3$ K), while at high temperature ($T > 10$ K) the molecular spin dynamics are governed by spin-phonon interactions.

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